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(54) **ORGANIC X-RAY DETECTOR AND X-RAY SYSTEMS**

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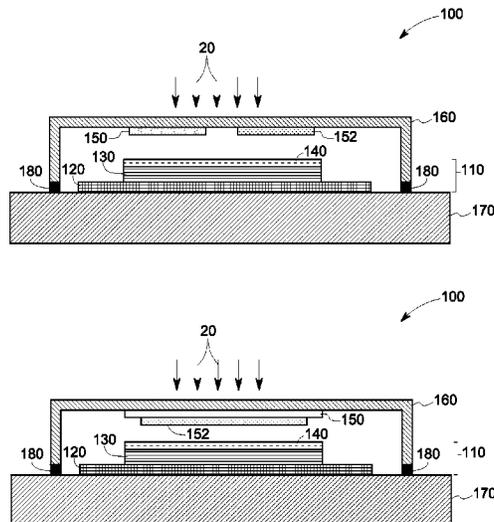
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(57) **ABSTRACT**

An organic x-ray detector is presented. The organic x-ray detector includes a layered structure. The layered structure includes a thin-film transistor (TFT) array disposed on a substrate, an organic photodiode disposed on the TFT array, and a scintillator layer disposed on the organic photodiode. The organic x-ray detector includes an encapsulation cover at least partially encapsulating the layered structure. The organic x-ray detector further includes at least one of a moisture getter layer and an oxygen getter layer disposed proximate to the organic photodiode, and in the path of an x-ray radiation incident on the layered structure. X-ray system including the organic x-ray detector is also presented.

20 Claims, 10 Drawing Sheets



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(52) **U.S. Cl.**
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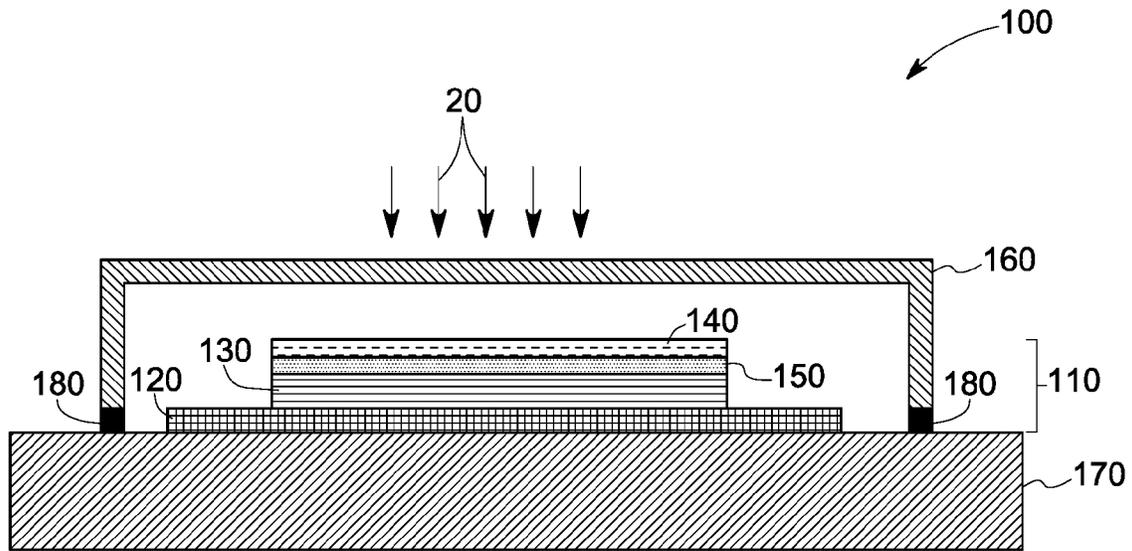


FIG. 1

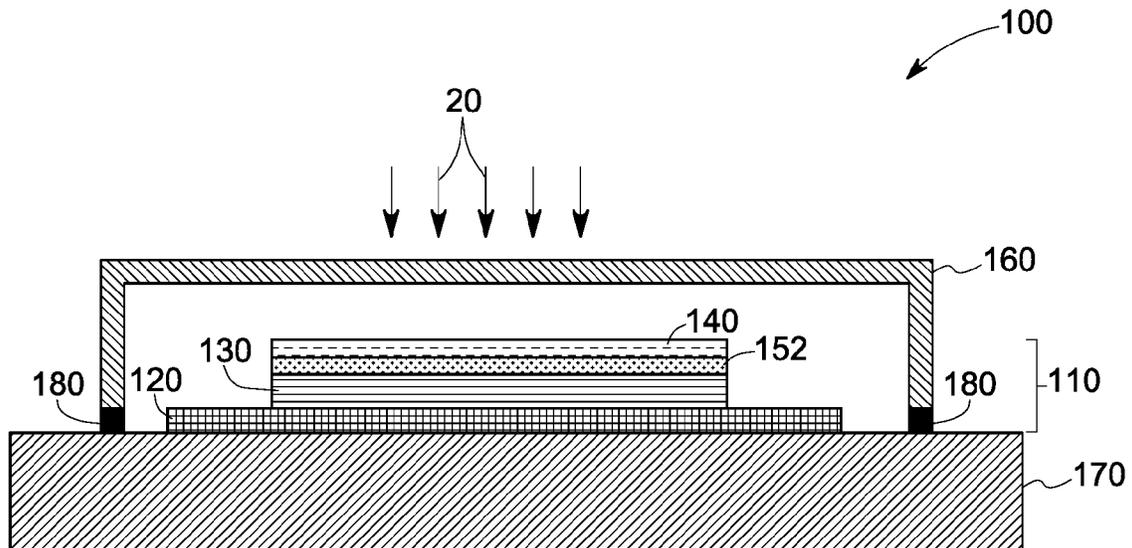


FIG. 2

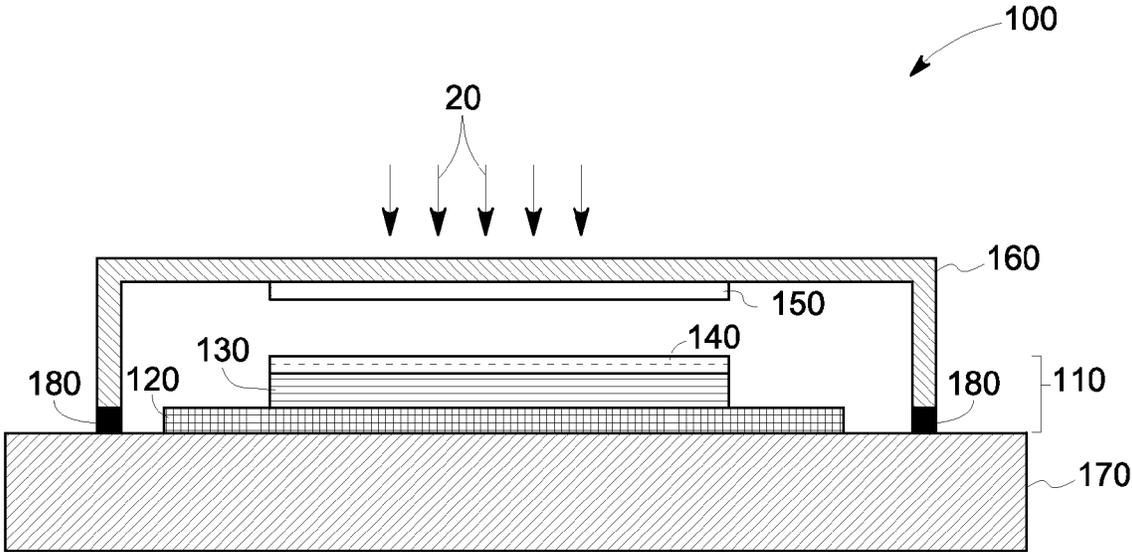


FIG. 3

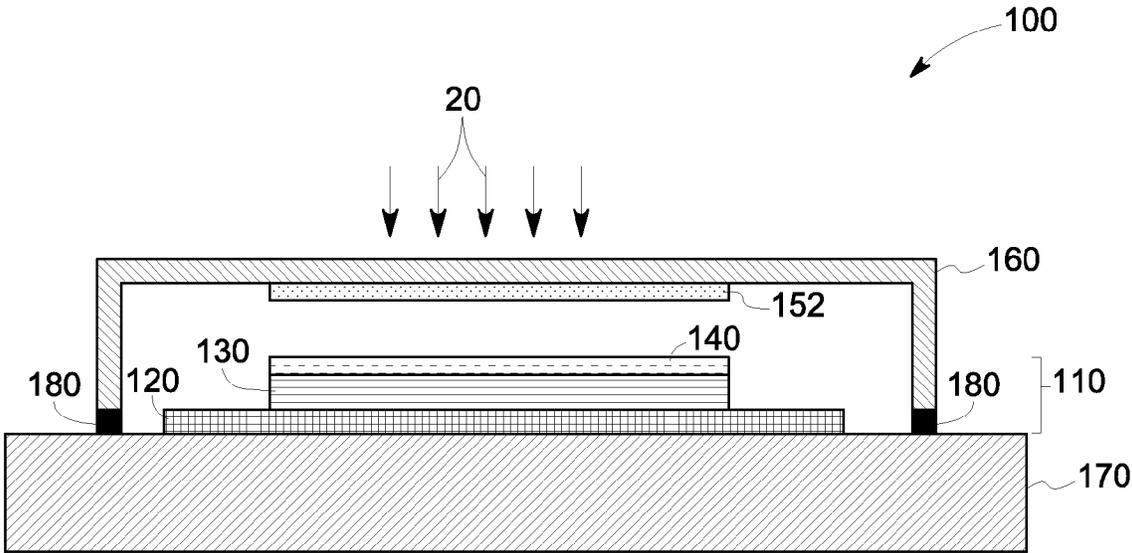


FIG. 4

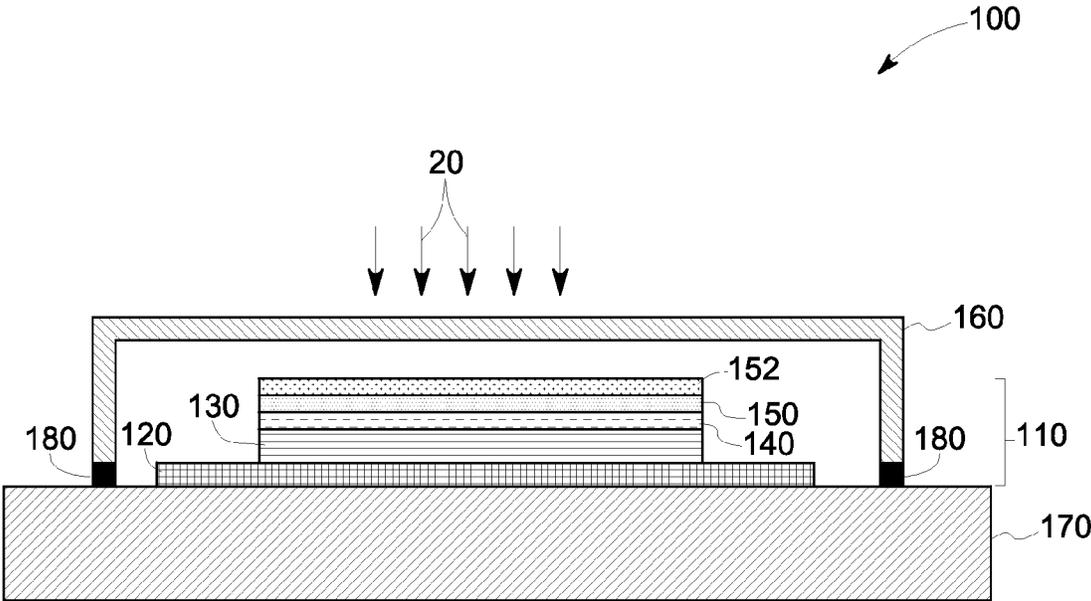


FIG. 5

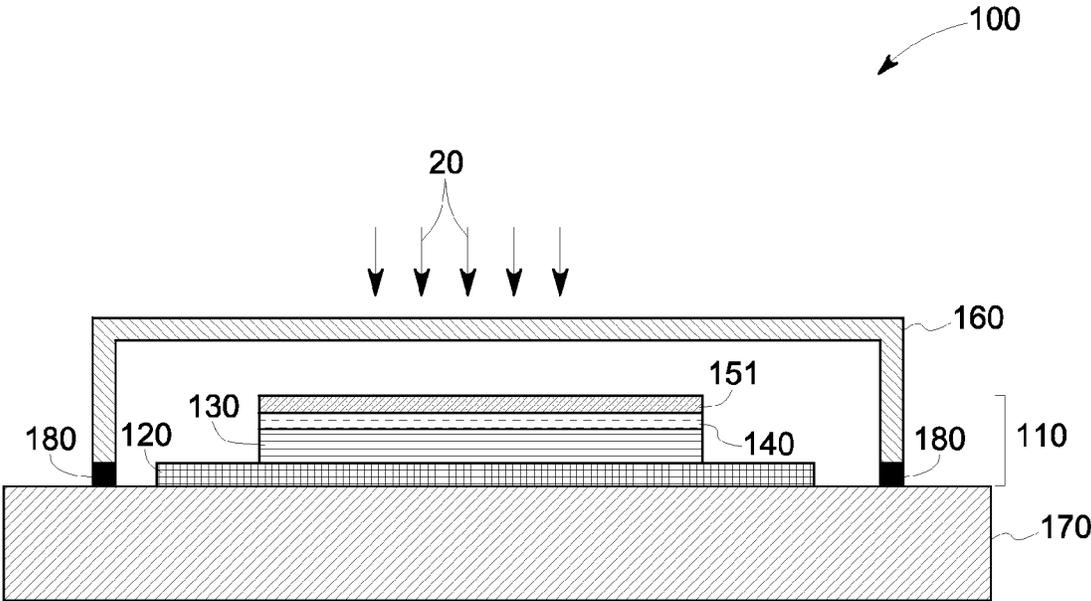


FIG. 6

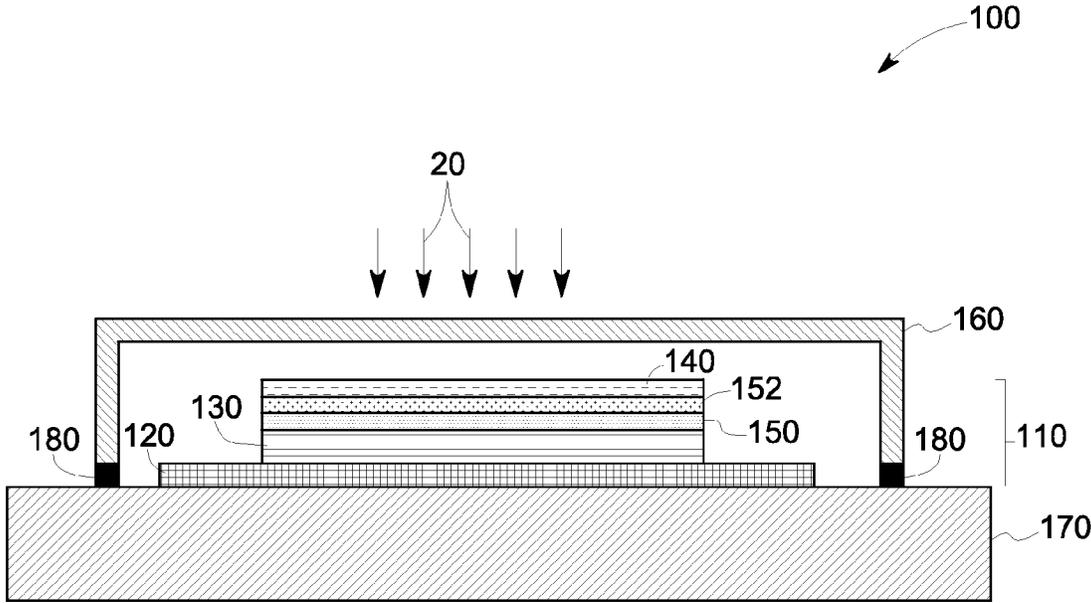


FIG. 7

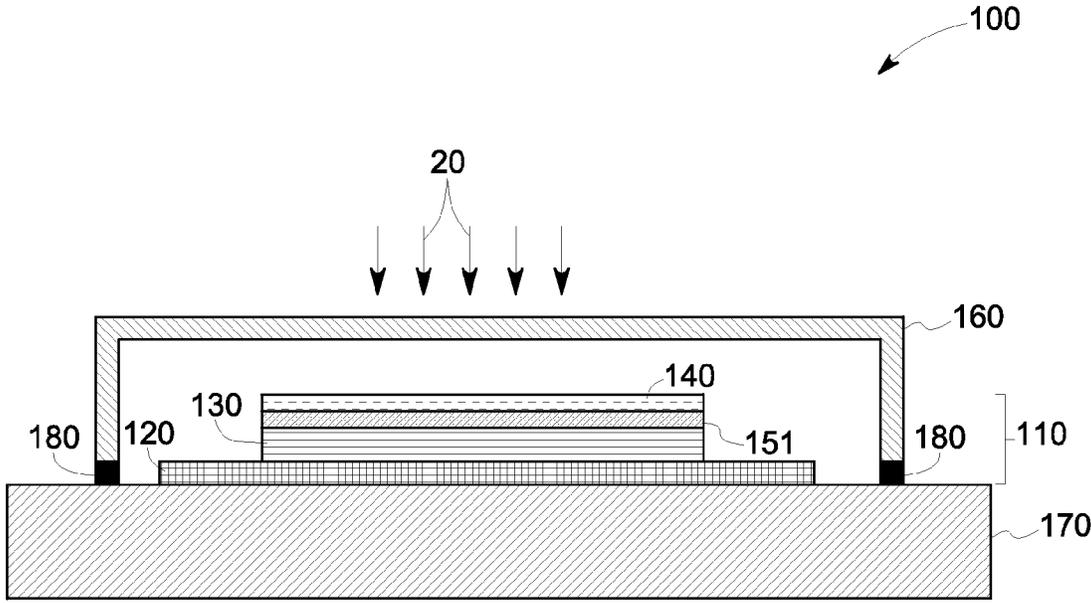


FIG. 8

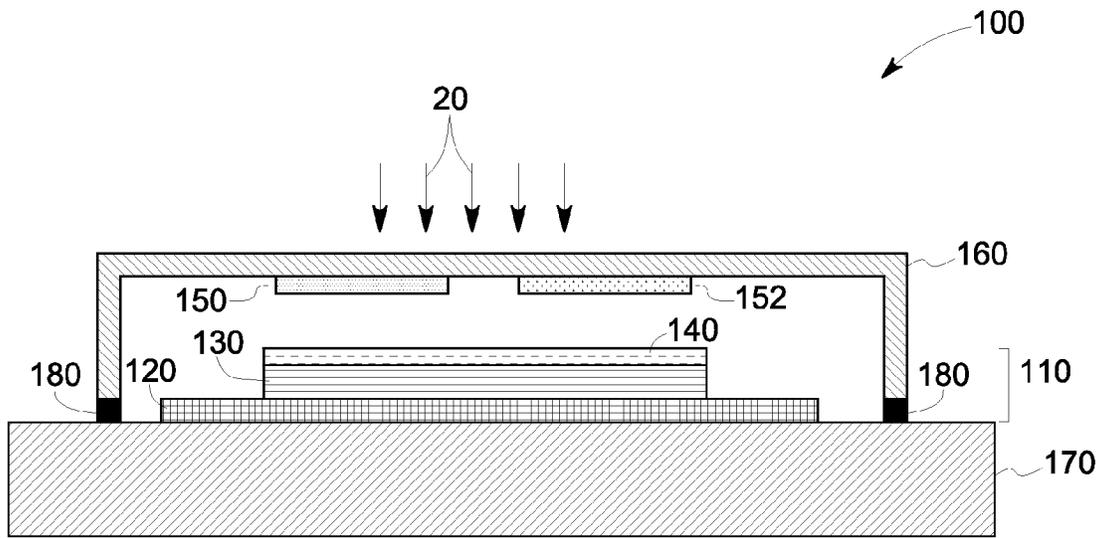


FIG. 9

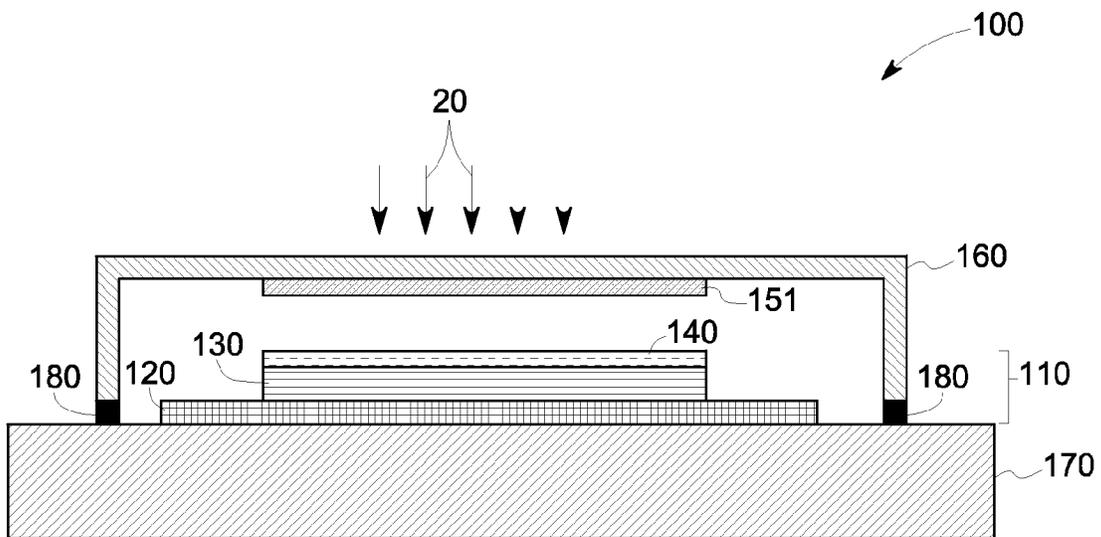


FIG. 10

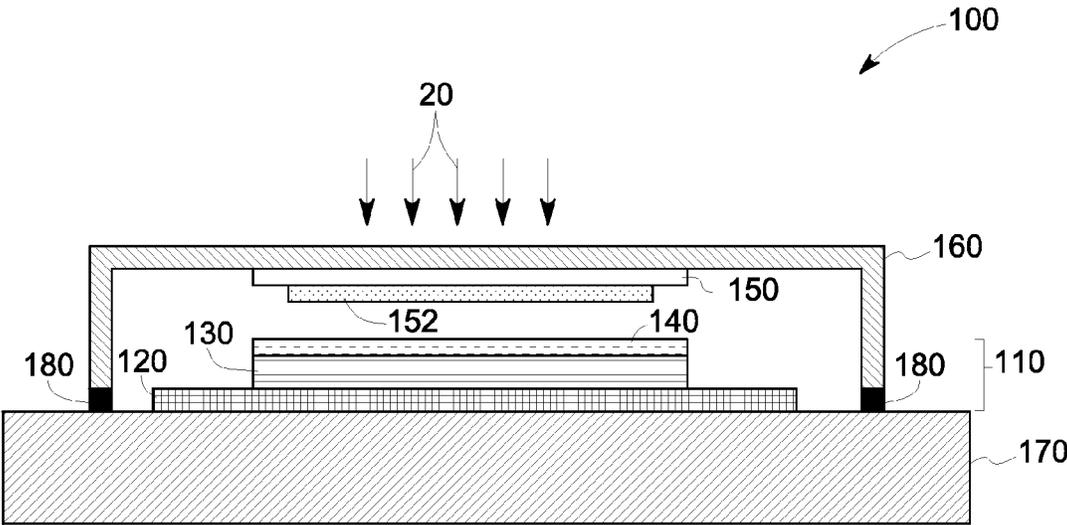


FIG. 11

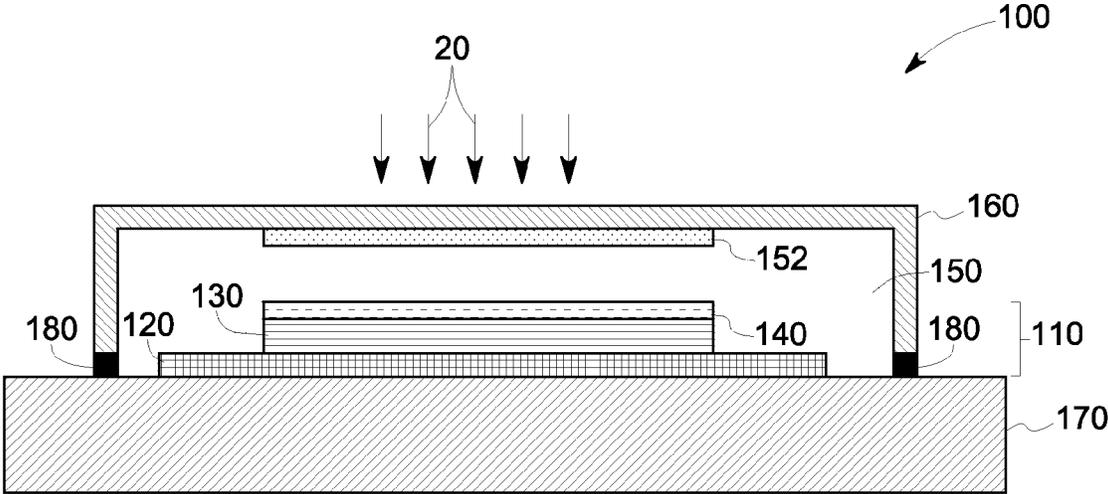


FIG. 12

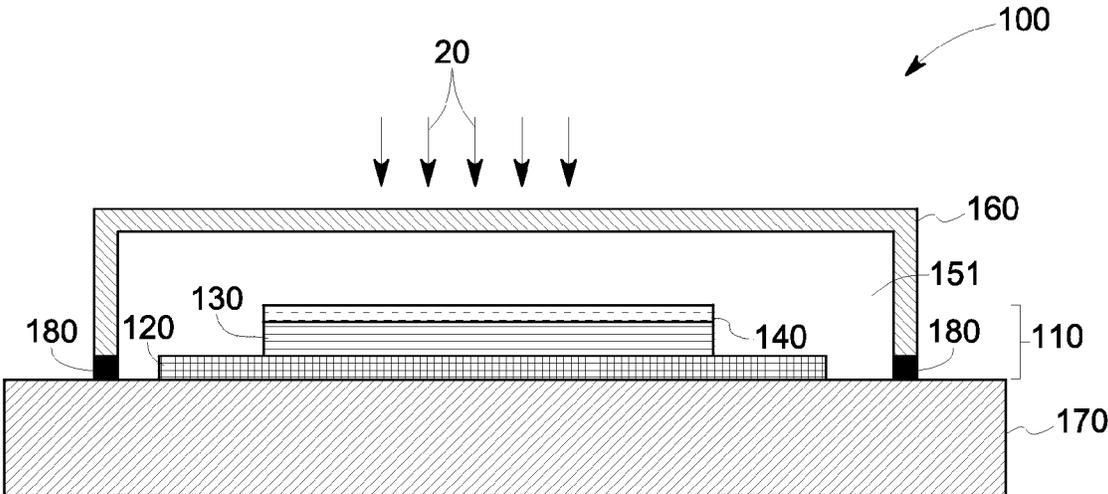


FIG. 13

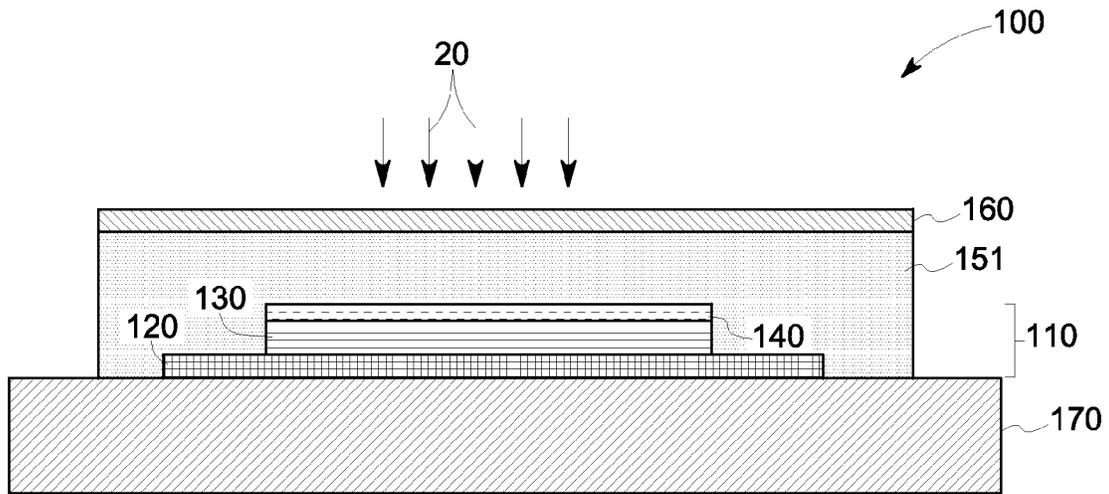


FIG. 14

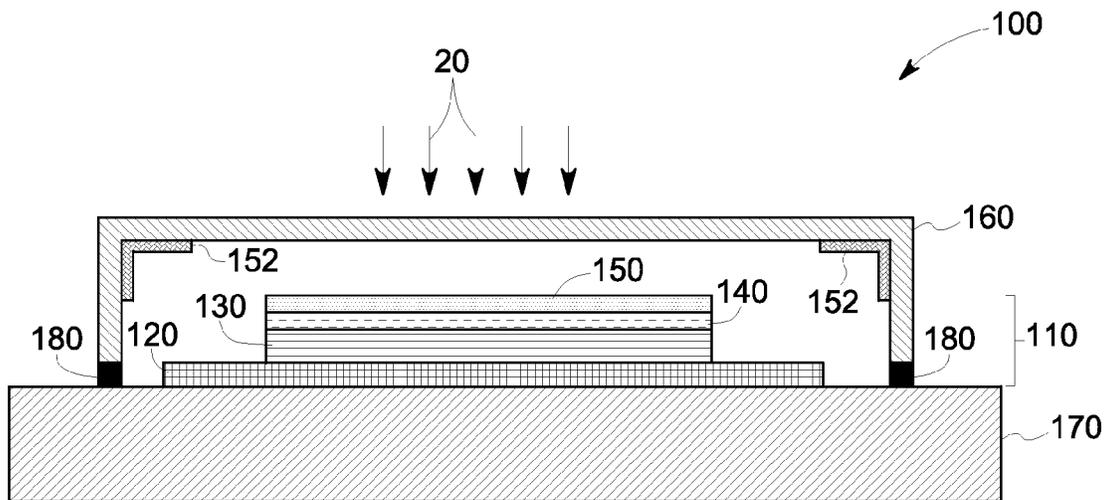


FIG. 15

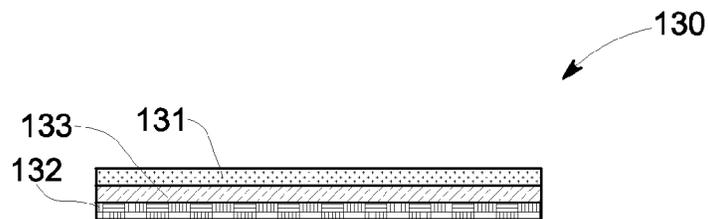


FIG. 16

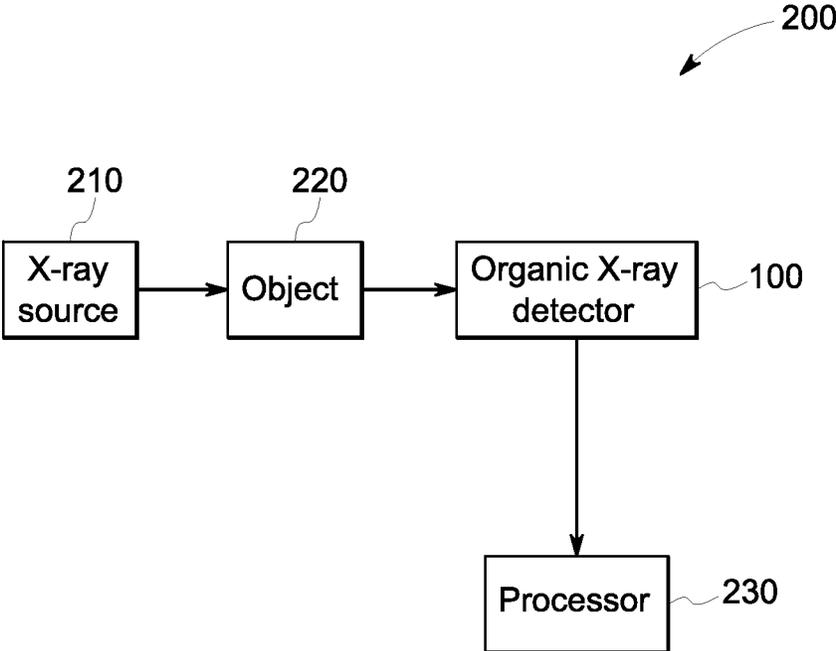


FIG. 17

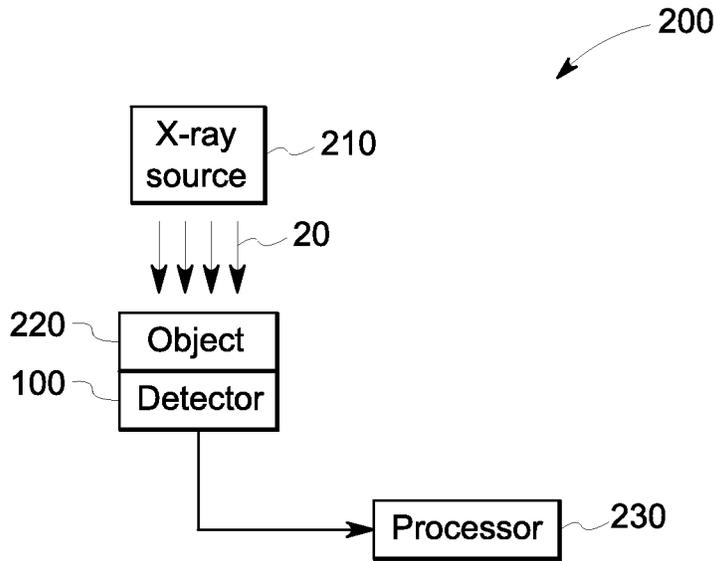


FIG. 18A

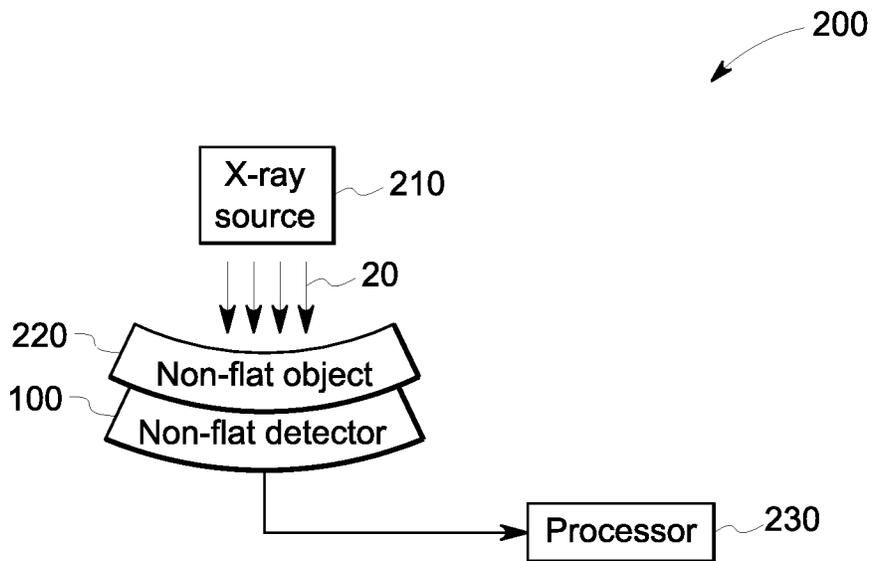


FIG. 18B

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ORGANIC X-RAY DETECTOR AND X-RAY SYSTEMS

BACKGROUND

Embodiments of the invention generally relate to organic x-ray detectors. More particularly, embodiments of the invention relate to organic x-ray detectors including oxygen and moisture getter layers.

Digital x-ray detectors fabricated with continuous photodiodes have potential applications for low cost digital radiography as well as for rugged, light-weight and portable detectors. Digital x-ray detectors with continuous photodiodes have an increased fill factor and potentially higher quantum efficiency. The continuous photodiode generally includes organic photodiodes (OPDs). A scintillator which converts x-ray to visible light is generally disposed on top of the OPDs.

Typical organic x-ray detectors are subject to performance degradation upon exposure to oxygen and/or moisture. Possible degradation mechanisms include one or both of oxidation of electrode materials and oxidation of organic materials (e.g., OPD materials). During the post OPD deposition process, such as, scintillator deposition, encapsulation, laser repair, or operation, OPD has a high chance of exposure to air. Most organic based photodiodes are sensitive to oxygen and/or moisture, and hence need to be protected from the oxygen-containing air. A hermetic seal is thus desirable to achieve a reliable OPD and organic x-ray detector. Typical x-ray detectors include a top cover along with edge seals. However, edge sealants are generally more permeable for moisture and oxygen than the top cover, and edge ingress of moisture/oxygen may be a limiting factor for long-term stability.

Therefore, there is a need for x-ray detector configurations with improved oxygen and moisture getter layers.

BRIEF DESCRIPTION

In one aspect, the invention relates to an organic x-ray detector. The organic x-ray detector includes a layered structure. The layered structure includes a thin-film transistor (TFT) array disposed on a substrate, an organic photodiode disposed on the TFT array, and a scintillator layer disposed on the organic photodiode. The organic x-ray detector includes an encapsulation cover at least partially encapsulating the layered structure. The organic x-ray detector further includes at least one of a moisture getter layer and an oxygen getter layer disposed proximate to the organic photodiode, and in the path of an x-ray radiation incident on the layered structure.

In another aspect, the invention relates to an organic x-ray detector including a layered structure. The layered structure includes a thin-film transistor (TFT) array disposed on a substrate, an organic photodiode disposed on the TFT array, and a scintillator layer disposed on the organic photodiode. The organic x-ray detector includes an encapsulation cover at least partially encapsulating the layered structure. The organic x-ray detector further includes an oxygen getter layer disposed between the organic photodiode and the scintillator layer in the layered structure; and a moisture getter layer disposed in contact with at least a portion of the encapsulation cover.

In yet another aspect, the invention relates to an x-ray system. The x-ray system includes an x-ray source; an organic x-ray detector; and a processor operable to process data from the organic x-ray detector. The organic x-ray

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detector includes a layered structure. The layered structure includes a thin-film transistor (TFT) array disposed on a substrate, an organic photodiode disposed on the TFT array, and a scintillator layer disposed on the organic photodiode.

The organic x-ray detector includes an encapsulation cover at least partially encapsulating the layered structure. The organic x-ray detector further includes at least one of a moisture getter layer and an oxygen getter layer disposed proximate to the organic photodiode, and in the path of an x-ray radiation incident on the layered structure.

These and other features, embodiments, and advantages of the present invention may be understood more readily by reference to the following detailed description.

DRAWINGS

These and other features, aspects, and advantages of the present invention will become better understood when the following detailed description is read with reference to the accompanying drawings, wherein:

FIG. 1 is a schematic of an organic x-ray detector, according to one embodiment of the invention;

FIG. 2 is a schematic of an organic x-ray detector, according to one embodiment of the invention;

FIG. 3 is a schematic of an organic x-ray detector, according to one embodiment of the invention;

FIG. 4 is a schematic of an organic x-ray detector, according to one embodiment of the invention;

FIG. 5 is a schematic of an organic x-ray detector, according to one embodiment of the invention;

FIG. 6 is a schematic of an organic x-ray detector, according to one embodiment of the invention;

FIG. 7 is a schematic of an organic x-ray detector, according to one embodiment of the invention;

FIG. 8 is a schematic of an organic x-ray detector, according to one embodiment of the invention;

FIG. 9 is a schematic of an organic x-ray detector, according to one embodiment of the invention;

FIG. 10 is a schematic of an organic x-ray detector, according to one embodiment of the invention;

FIG. 11 is a schematic of an organic x-ray detector, according to one embodiment of the invention;

FIG. 12 is a schematic of an organic x-ray detector, according to one embodiment of the invention;

FIG. 13 is a schematic of an organic x-ray detector, according to one embodiment of the invention;

FIG. 14 is a schematic of an organic x-ray detector, according to one embodiment of the invention;

FIG. 15 is a schematic of an organic x-ray detector, according to one embodiment of the invention;

FIG. 16 is a schematic of an organic photodiode, according to one embodiment of the invention;

FIG. 17 is schematic of an x-ray system, according to one embodiment of the invention;

FIG. 18A is schematic of an x-ray system, according to one embodiment of the invention; and

FIG. 18B is schematic of an x-ray system, according to one embodiment of the invention.

DETAILED DESCRIPTION

In the following specification and the claims, which follow, reference will be made to a number of terms, which shall be defined to have the following meanings. The singular forms "a", "an" and "the" include plural referents unless the context clearly dictates otherwise. "Optional" or "optionally" means that the subsequently described event or

circumstance may or may not occur, and that the description includes instances where the event occurs and instances where it does not.

Approximating language, as used herein throughout the specification and claims, may be applied to modify any quantitative representation that could permissibly vary without resulting in a change in the basic function to which it is related. Accordingly, a value modified by a term or terms, such as “about”, and “substantially” is not to be limited to the precise value specified. In some instances, the approximating language may correspond to the precision of an instrument for measuring the value. Similarly, “free” may be used in combination with a term, and may include an insubstantial number, or trace amounts, while still being considered free of the modified term. Here and throughout the specification and claims, range limitations may be combined and/or interchanged, such ranges are identified and include all the sub-ranges contained therein unless context or language indicates otherwise.

As used herein, the term “layer” refers to a material disposed on at least a portion of an underlying surface in a continuous or discontinuous manner. Further, the term “layer” does not necessarily mean a uniform thickness of the disposed material, and the disposed material may have a uniform or a variable thickness. As used herein, the term “disposed on” refers to layers disposed directly in contact with each other or indirectly by having intervening layers there between, unless otherwise specifically indicated. The term “adjacent” as used herein means that the two layers are disposed contiguously and are in direct contact with each other.

In the present disclosure, when a layer is being described as “on” another layer or substrate, it is to be understood that the layers can either be directly contacting each other or have one (or more) layer or feature between the layers. Further, the term “on” describes the relative position of the layers to each other and does not necessarily mean “on top of” since the relative position above or below depends upon the orientation of the device to the viewer. Moreover, the use of “top,” “bottom,” “above,” “below,” and variations of these terms is made for convenience, and does not require any particular orientation of the components unless otherwise stated.

Electro-optical devices, such as, but not limited to, organic x-ray detectors include an electronically or optically active portion—e.g., scintillators and photodiodes that are frequently disposed on a substrate. In order to protect the active portion and the substrate from degradation due to exposure to moisture, oxygen, or corrosive chemical attack, the electro-optical devices are normally encased in a seal. Typical x-ray detectors include a top cover along with edge seals. However, edge sealants are generally more permeable for moisture and oxygen than the top cover, and edge ingress of moisture/oxygen may be a limiting factor for long-term stability.

One aspect of the invention is to provide an electro-optical device, such as, but not limited to, organic x-ray detectors. A schematic representation of such an organic x-ray detector (XRD) is shown in FIGS. 1-15. As shown in FIGS. 1-15, an organic x-ray detector **100** includes a layered structure **110**. The layered structure **110** includes a thin-film transistor (TFT) array **120** disposed on a substrate **170**, an organic photodiode **130** disposed on the TFT array **120**, and a scintillator layer **140** disposed on the organic photodiode **130**. The organic x-ray detector **100** further includes an encapsulation cover **160** at least partially encapsulating the layered structure **110**. The organic x-ray detector **100** further

includes at least one of a moisture getter layer and an oxygen getter layer disposed proximate to the organic photodiode **130**, and in the path of an x-ray radiation **20** incident on the layered structure **110**.

As illustrated in FIGS. 1-15, the scintillator layer **140** is excited by impinging x-ray radiation **20** and produces visible light. Scintillator layer **140** may be composed of a phosphor material that is capable of converting x-rays to visible light. The wavelength region of light emitted by scintillator layer **140** may range from about 360 nm to about 830 nm. Suitable materials for the scintillator layer **140** include, but are not limited to, cesium iodide (CsI), CsI (TI) (cesium iodide to which thallium has been added) and terbium-activated gadolinium oxysulfide (GOS). Such materials are commercially available in the form of a sheet or screen. Another scintillator that may be used is a PIB (particle in binder) scintillator, where scintillating particles may be incorporated in a binder matrix material and flattened on a substrate. The scintillator layer **140** may be a monolithic scintillator or pixelated scintillator array. The visible light generated by the scintillator layer **140** irradiates an organic photodiode **130** disposed on a TFT array **120**.

As shown in FIG. 16, the organic photodiode **130** includes a first electrode **131**, a second electrode **132**, and an absorber layer (sometimes also referred to as an “active layer”) **133** interposed between the first electrode **131** and the second electrode **132**. Depending on the application and variations in design, the absorber layer **133** may include a single organic layer or may include multiple organic layers. Further, the organic photodiode **130** may be directly disposed on the TFT array **120** or the design may include one or more layers disposed between the organic photodiode **130** and the TFT array **120**.

The absorber layer **133** may be a bulk, hetero junction organic photodiode layer that absorbs light, separates charge and transports holes and electrons to the contact layers. In some embodiments, the absorber layer **133** may be patterned. Absorber layer **133** may include a blend of a donor material and an acceptor material; more than one donor material or acceptor material may be included in the blend. In some embodiments, the donor and acceptor may be incorporated in the same molecule. Further, the HOMO/LUMO levels of the donor and acceptor materials may be compatible with that of the first electrode **131** and second electrode **132** in order to allow efficient charge extraction without creating an energetic barrier.

Suitable donor materials include low bandgap polymers having LUMO ranging from about 1.9 eV to about 4.9 eV, particularly from 2.5 eV to 4.5 eV, more particularly from 3.0 eV to 4.5 eV; and HOMO ranging from about 2.9 eV to about 7 eV, particularly from 4.0 eV to 6 eV, more particularly from 4.5 eV to 6 eV. The low band gap polymers include conjugated polymers and copolymers composed of units derived from substituted or unsubstituted monoheterocyclic and polyheterocyclic monomers such as thiophene, fluorene, phenylenevinylene, carbazole, pyrrolopyrrole, and fused heteropolycyclic monomers containing the thiophene ring, including, but not limited to, thienothiophene, benzodithiophene, benzothiadiazole, pyrrolothiophene monomers, and substituted analogs thereof. In particular embodiments, the low band gap polymers comprise units derived from substituted or unsubstituted thienothiophene, benzodithiophene, benzothiadiazole, carbazole, isothianaphthene, pyrrole, benzo-bis(thiadiazole), thienopyrazine, fluorene, thiazoloquinoxaline, or combinations thereof. In the context of the low band gap polymers described herein, the term “units derived from” means that the units are each a residue

comprising the monoheterocyclic and polyheterocyclic group, without regard to the substituents present before or during the polymerization; for example, "the low band gap polymers comprise units derived from thienothiophene" means that the low band gap polymers comprise divalent thienothiophenyl groups. Examples of suitable materials for use as low bandgap polymers in the organic x-ray detectors according to the present invention include copolymers derived from substituted or unsubstituted thienothiophene, benzodithiophene, benzothiadiazole or carbazole monomers, and combinations thereof, such as poly[[4,8-bis(2-ethyl hexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl (PTB7), 2,1,3-benzothiadiazole-4,7-diyl[4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2,6-diyl (PCPDTBT), poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT), poly[(4,40-bis(2-ethylhexyl)dithieno[3,2-b:20,30-d]silole)-2,6-diyl-alt-(2,1,3-benzo-thiadiazole)-4,7-diyl] (PSBTBT), poly((4,8-bis(octyloxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)(2-((dodecyloxy)carbonyl)thieno(3,4-b)thiophenediyl)) (PTB1), poly((4,8-bis(octyloxy)benzo(1,2-b:4,5-b')dithiophene-2,6-diyl)(2-((ethylhexyloxy)carbonyl)thieno(3,4-b)thiophenediyl)) (PTB2), poly((4,8-bis(octyl)benzo(1,2-b:4,5-b')dithiophene-2,6-diyl) (2-((ethylhexyloxy)carbonyl)thieno(3,4-b)thiophenediyl)) (PTB3), poly((4,8-bis(ethylhexyloxy)benzo(1,2-b:4,5-b')dithiophene-2,6-diyl)(2-((octyloxy)carbonyl)-3-fluoro)thieno(3,4-b)thiophenediyl)) (PTB4), poly((4,8-bis(ethylhexyloxy)benzo(1,2-b:4,5-b')dithiophene-2,6-diyl)(2-((octyloxy)carbonyl)thieno(3,4-b)thiophenediyl)) (PTB5), poly((4,8-bis(octyloxy)benzo(1,2-b:4,5-b')dithiophene-2,6-diyl)(2-((butyloxy)carbonyl)thieno(3,4-b)thiophenediyl)) (PTB6), poly[[5-(2-ethylhexyl)-5,6-dihydro-4,6-dioxo-4H-thieno[3,4-c]pyrrole-1,3-diyl][4,8-bis R2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl]] (PBDTTPD), poly[1-(6-{4,8-bis R2-ethylhexyl)oxy}1-6-methylbenzo[1,2-b:4,5-b']dithiophen-2-yl)-3-fluoro-4-methylthieno[3,4-b]thiophen-2-yl)-1-octanone] (PBDTTP-CF), and poly[2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl(9,9-dioctyl-9H-9-silafluorene-2,7-diyl)-2,5-thiophenediyl] (PSiF-DBT). Other suitable materials are poly[5,7-bis(4-decanyl-2-thienyl)thieno[3,4-b]dithiazole-thiophene-2,5] (PDDTT), poly[2,3-bis(4-(2-ethylhexyloxy)phenyl)-5,7-di(thiophen-2-yl)thieno[3,4-b]pyrazine] (PDTTP), and polythieno[3,4-b]thiophene (PTT). In particular embodiments, suitable materials are copolymers derived from substituted or unsubstituted benzodithiophene monomers, such as the PTB1-7 series and PCPDTBT; or benzothiadiazole monomers, such as PCDTBT and PCPDTBT.

In particular embodiments, the donor material is a polymer with a low degree of crystallinity or is an amorphous polymer. Degree of crystallinity may be increased by substituting aromatic rings of the main polymer chain. Long chain alkyl groups containing six or more carbons or bulky polyhedral oligosilsesquioxane (POSS) may result in a polymer material with a lower degree of crystallinity than a polymer having no substituents on the aromatic ring, or having short chain substituents such as methyl groups. Degree of crystallinity may also be influenced by processing conditions and means, including, but not limited to, the solvents used to process the material and thermal annealing conditions. Degree of crystallinity is readily determined using analytical techniques such as calorimetry, differential scanning calorimetry, x-ray diffraction, infrared spectroscopy and polarized light microscopy.

Suitable materials for the acceptor material include fullerene derivatives such as [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM), PCBM analogs such as PC₇₀BM, PC₇₁BM, PC₈₀BM, bis-adducts thereof, such as bis-PC₇₁BM, indene mono-adducts thereof, such as indene-C₆₀ monoadduct (ICMA) and indene bis-adducts thereof, such as indene-C₆₀ bisadduct (ICBA). Fluorene copolymers such as poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-(4,7-bis(3-hexylthiophen-5-yl)-2,1,3-benzothiadiazole)-2',2''-diyl] (F8TBT) may also be used, alone or with a fullerene derivative.

In one embodiment, the first electrode **131** functions as a cathode and the second electrode **132** as an anode. In another embodiment, the first electrode **131** functions as an anode and the second electrode **132** as a cathode. Suitable anode materials include, but are not limited to, metals such as Al, Ag, Au, and Pt, metal oxides such as indium tin oxide (ITO), indium zinc oxide (IZO), and zinc oxide (ZnO), and organic conductors such as p-doped conjugated polymers like PEDOT. Suitable cathode materials include transparent conductive oxides (TCO) and thin films of metals such as gold and silver. Examples of suitable TCO include ITO, IZO, aluminum zinc oxide (AZO), fluorinated tin oxide (FTO), tin oxide (SnO₂), titanium dioxide (TiO₂), ZnO, indium zinc oxide (In—Zn—O series), indium gallium oxide, gallium zinc oxide, indium silicon zinc oxide, indium gallium zinc oxide, or combinations thereof.

Referring again to FIGS. 1-15, the TFT array **120** may be a two dimensional array of passive or active pixels, which stores charge for read out by electronics, disposed on an active layer formed of amorphous silicon or an amorphous metal oxide, or organic semiconductors. In some embodiments, the TFT array **120** includes a silicon TFT array, an oxide TFT array, an organic TFT, or combinations thereof. Suitable amorphous metal oxides include zinc oxide, zinc tin oxide, indium oxides, indium zinc oxides (In—Zn—O series), indium gallium oxides, gallium zinc oxides, indium silicon zinc oxides, and indium gallium zinc oxides (IGZO). IGZO materials include InGaO₃(ZnO)_m, where m is <6 and InGaZnO₄. Suitable organic semiconductors include, but are not limited to, conjugated aromatic materials, such as rubrene, tetracene, pentacene, perylene diimides, tetracyanoquinodimethane and polymeric materials such as polythiophenes, polybenzodithiophenes, polyfluorene, polydiacetylene, poly(2,5-thiophenylene vinylene), poly(p-phenylene vinylene) and derivatives thereof.

The TFT array **120** is further disposed on a substrate **170**. Suitable substrate **170** materials include glass, ceramics, plastics and metals. The substrate **170** may be present as a rigid sheet such as a thick glass, a thick plastic sheet, a thick plastic composite sheet, and a metal plate; or a flexible sheet, such as, a thin glass sheet, a thin plastic sheet, a thin plastic composite sheet, and metal foil. Examples of suitable materials for the substrate **170** include glass, which may be rigid or flexible; plastics such as polyethylene terephthalate, polybutylene phthalate, polyethylene naphthalate, polystyrene, polycarbonate, polyether sulfone, polyallylate, polyimide, polycycloolefin, norbornene resins, and fluoropolymers; metals such as stainless steel, aluminum, silver and gold; metal oxides such as titanium oxide and zinc oxide; and semiconductors such as silicon. In one particular embodiment, the substrate includes a polycarbonate.

As shown in FIGS. 1-15, the scintillator layer **140**, the organic photodiode **130**, and the TFT array **120** are enclosed inside an encapsulation cover **160** to protect them from the moisture and oxygen introduced from the atmosphere. In some embodiments, one or more additional seals **180** may be

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provided to provide effective sealing between the encapsulation cover **160** and the substrate **170**.

In some embodiments of the invention, apart from being protected from the external moisture and oxygen, the organic photodiode **130** may be further protected from the oxygen and/or moisture that may be introduced (for example, from the scintillator layer **140**) during the formation of the organic x-ray detector **100** or during operation of the organic x-ray detector **100**.

At least one of an oxygen getter layer and a moisture getter layer may be further provided in the organic x-ray detector **100** to provide this protection. The oxygen getter layer and the moisture getter layers are disposed proximate to the organic photodiode **130**. The term "disposed proximate" as used herein means that the oxygen and moisture getter layers are either disposed directly in contact with the organic photodiode **130**; or at a distance such that the organic photodiode **130** is protected from exposure to oxygen and/or moisture because of the oxygen and moisture getter layers. Further, the oxygen and the moisture getter layers are disposed in the path of an x-ray radiation **20** incident on the layered structure **110** such that the x-ray radiation **20** passes through at least a portion of the oxygen and getter layers before reaching the organic photodiode **130**.

The moisture getter layer may include any suitable material selected from the group consisting of alkali metals, alkaline earth metals, alkali metal oxides, alkaline earth metal oxides, aluminum oxide, zeolite, silica, and combinations thereof. Non limiting examples of suitable alkaline metals include calcium, barium, or combinations thereof. Not limiting examples of suitable oxides include calcium oxide, barium oxide, aluminum oxide, or combinations thereof.

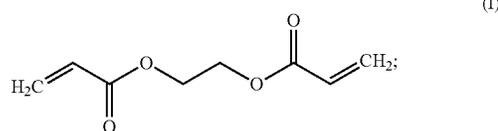
The oxygen getter layer may include any suitable material selected from the group consisting of ether-containing materials, ascorbic acids, polyhydric alcohols, alkylene glycols, and combinations thereof. In certain embodiments, the oxygen getter layer includes an ether-containing material. Non-limiting examples of suitable ether-containing materials include polyethers, crown ethers, epoxy resins, or combinations thereof. In some embodiments, the ether-containing material may include a polymer that includes a polyether moiety. The polyether moiety may be present as a homopolymer, as a block in a block copolymer, or as a side chain on another polymer (i.e. as a comb polymer). There is no limitation on the polymer morphology, that is, the polymers may be linear, branched, crosslinked, networked, or cyclic. Further, any suitable molecular weight may be used such that a liquid or a solid material can be obtained. Also, as the oxidation mechanism is independent of endgroup chemistry, there is no limitation on endgroup chemistry, and the nature of the two endgroups can be different. For example, one or both endgroups may be hydrogen, methyl, higher alkyl, vinyl, epoxy, thiol, glycidyl, tosylate, or an ester. The ester could be an acrylate or a methacrylate, thereby allowing polymerization of the polyether moiety either by itself or as a mixture with other monomers.

In some embodiments, the ether-containing material includes a poly(alkylene glycol), such as, for example, poly(ethylene glycol), poly(propylene glycol), poly(butylene glycol), or combinations thereof.

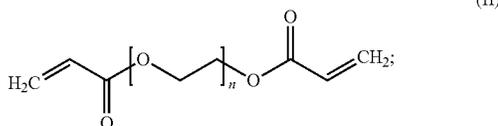
In some embodiments, the ether-containing material includes bifunctional ethylene glycol or poly(ethylene glycol). Non-limiting examples of suitable ether-containing materials include:

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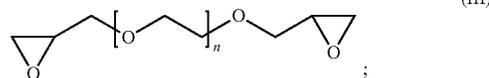
ethylene glycol diacrylate having a chemical structure (I):



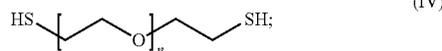
poly(ethylene glycol)diacrylate having a chemical structure (II):



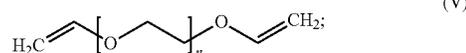
poly(ethylene glycol)diglycidyl ether having a chemical structure (III):



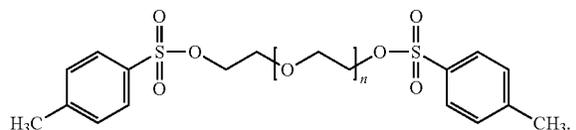
poly(ethylene glycol)dithiol having a chemical structure (IV):



poly(ethylene glycol)divinyl ether having a chemical structure (V):



or poly(ethylene glycol)-di-tosylate having a chemical structure (VI):



Crosslinking promoters such as photoinitiators, thermal initiators, radical initiators, photo-acid generators, and photo-base generators may be further added to the bifunctional ether-containing material to initiate cross-linking reactions and/or enhance the degree of cross-linking. Non-limiting examples of suitable promoters include ethylbenzoyl ether, isopropylbenzoyl ether, α -methylbenzoyl ethyl ether, benzoyl phenyl ether, α -acyloxime ester, α,α -diethoxy acetophenone, 1,1-dichloroacetophenone, 2-hy-

droxy-2-methyl-1-phenylpropane-1-one [Darocure 1173 of Ciba Specialty Chemicals], 1-hydroxycyclohexyl phenyl ketone [Irgacure 184, Darocure 1116, Irgacure 907 of Ciba Specialty Chemicals], bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (Irgacure 819 of Ciba Specialty Chemicals), anthraquinone, 2-ethyl anthraquinone, 2-chloro anthraquinone, thioxanthone, isopropyl thioxanthone, chlorothioxanthone, benzophenone, p-chlorobenzophenone, benzyl benzoate, benzoyl benzoate and Michler's ketone. Non-limiting examples of suitable thermal initiators include azoisobutyronitrile-based and peroxide-based initiators.

In some embodiments, the ether-containing material may be used in essentially pure form relying on adventitious radicals or x-rays to create the free radicals that can react with oxygen. Alternatively, a catalyst may be further used to generate radicals. Effective catalysts generally have a plurality of oxidation states readily available and include transition metals such as iron, cobalt, and copper.

In some embodiments, the oxygen-getter layer may further include a transition metal catalyst, for example, a cobalt salt, an iron salt, a copper salt, or combinations thereof. The transition metals may be introduced as salts of carboxylic acids to give good compatibility with the polyether. Non-limiting examples of suitable catalysts include copper acetate, copper octanoate, cobalt acetate, cobalt octanoate, or combinations thereof.

As mentioned previously, a layer includes material disposed on at least a portion of an underlying surface in a continuous or discontinuous manner. Further, the term "layer" does not necessarily mean a uniform thickness of the disposed material, and the disposed material may have a uniform or a variable thickness. In some embodiments, one or both of the oxygen getter layer and the moisture getter layer may have any suitable shape, non-limiting examples of which include a continuous layer, a strip, a patch, or combinations thereof. Further, one or both of the oxygen getter layer and the moisture getter may be primarily comprised of the suitable getter material; or alternately may further include a binder and the getter material may be dispersed in the binder.

FIGS. 1-4 illustrate embodiments including an oxygen getter layer 150 or a moisture getter layer 152. In FIGS. 1 and 2, the oxygen getter layer 150 or the moisture getter layer 152 is disposed in the layered structure 110. In alternate embodiments, the oxygen getter layer 150 or the moisture getter layer 152 is disposed in contact with at least a portion of the encapsulation cover 160, as shown in FIGS. 3 and 4.

In some embodiments as shown in FIGS. 5-15, the organic x-ray detector 100 includes both the oxygen getter layer 150 and the moisture getter layer 152. The oxygen-getter layer 150 and the moisture getter layer 152 may have any suitable configuration in the organic x-ray detector 100 provided that the getter layers are disposed in the path of the x-ray radiation 20. In some embodiments, the moisture getter layer 152 and the oxygen getter layer 150 may be disposed as two separate layers 150, 152, as shown in FIGS. 5, 7, 9, 11, 12 and 15. In some other embodiments, the moisture getter layer 152 and the oxygen getter layer 150 are disposed as a single layer 151, as shown in FIGS. 6, 8, 10, 13 and 14.

Further, at least one of the oxygen getter layer 150 and the moisture getter layer 152 may be a component of the layered structure 110, as shown in FIGS. 5-8. Alternately, at least one of the oxygen getter layer 150 and the moisture getter layer 152 may be disposed such that at least a portion of the oxygen getter layer 150 or the moisture getter layer 152 is in contact with the encapsulation cover 160, as shown in FIGS. 9-15.

In some embodiments, the layered structure 110 includes at least one of the moisture getter layer 152 and the oxygen getter layer 150. In some embodiments, the layered structure 110 includes both the moisture getter layer 152 and the oxygen getter layer 150. In some instances wherein the layered structure 110 includes the getter layer, at least one of the moisture getter layer 152 and the oxygen getter layer 150 may be interposed between the organic photodiode 130 and the scintillator layer 140. In other instances, at least one of the moisture getter layer 152 and the oxygen getter layer 150 may be disposed on the scintillator layer 140. the moisture getter layer and the oxygen getter layer may be disposed on the scintillator layer.

FIG. 5 illustrates an embodiment of an organic x-ray detector 100 wherein the oxygen getter layer 150 is disposed on top of the scintillator layer 140 and the moisture getter layer 152 is disposed on the oxygen getter layer 150. In other embodiments (not shown in Figures), the moisture getter layer 152 may be disposed on top of the scintillator layer 140, and the oxygen getter layer 150 may be disposed on the moisture getter layer 152. FIG. 6 illustrates an alternative embodiment of an organic x-ray detector 100 wherein the oxygen getter layer 150 and the moisture getter layer 152 are disposed as a single layer 151 on the scintillator layer 140.

FIG. 7 illustrates an embodiment of an organic x-ray detector 100 wherein the oxygen and moisture getter layers 150, 152 are interposed between the scintillator layer 140 and the organic photodiode 130. In the embodiment illustrated in FIG. 7, the oxygen getter layer 150 is disposed on the organic photodiode 130, and the moisture getter layer 152 is disposed on the oxygen getter layer 150. In other embodiments (not shown in Figures), the moisture getter layer 152 may be disposed on the organic photodiode 130, and the oxygen getter layer 150 may be disposed on the moisture getter layer 152. FIG. 8 illustrates an alternative embodiment of an organic x-ray detector 100 wherein the oxygen getter layer 150 and the moisture getter layer 152 are disposed as a single layer 151 between the organic photodiode 130 and the scintillator layer 140.

In some other embodiments, at least one of the moisture getter layer 152 and the oxygen getter layer 150 is disposed in contact with at least a portion of the encapsulation cover 160. In some such instances, both the moisture getter layer 152 and the oxygen getter layer 150 are disposed in contact with at least a portion of the encapsulation cover 160. Further, in some such instances, at least one of the moisture getter layer 152 and the oxygen getter layer 150 substantially encapsulates the layered structure 110.

FIG. 9 illustrates an embodiment of an organic x-ray detector 100 wherein both the oxygen getter layer 150 and the moisture getter layer 152 are disposed in contact with at least a portion of the encapsulation cover 160. FIG. 10 illustrates an alternate embodiment of an organic x-ray detector 100, wherein the oxygen getter layer 150 and the moisture getter layer 152 are disposed as a single layer 151 in contact with at least a portion of the encapsulation cover 160. FIG. 11 illustrates an embodiment of an organic x-ray detector 100 wherein the oxygen getter layer 150 is disposed in contact with at least a portion of the encapsulation cover 160 and the moisture getter layer 152 is disposed in contact with the oxygen getter layer 150.

FIG. 12 illustrates an embodiment of an organic x-ray detector 100 wherein the oxygen getter layer 150 substantially encapsulates the layered structure 110, and the moisture getter layer 152 is disposed in contact with at least a portion of the encapsulation cover 160. FIG. 13 illustrates an alternate embodiment of an organic x-ray detector 100, wherein the oxygen getter layer 150 and the moisture getter layer 152 are disposed as a single layer 151 substantially encapsulating the layered structure 110. In FIG. 13, the

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encapsulation cover **160** and the seals **180** may further provide a sealing arrangement from the outside environment. Alternately, as shown in FIG. **14**, the single layer **151** itself may provide sealing from the outside environment.

FIG. **15** illustrates another embodiment of an organic x-ray detector **100** including an oxygen getter layer **150** and a moisture getter layer **152**. As shown in FIG. **15**, the layered structure **110** includes the oxygen getter layer **150** and the moisture getter layer **152** is disposed in contact with at least a portion of the encapsulation cover **160**.

Without being bound by any theory it is believed that the incorporation of the oxygen getter layer **150** and the moisture getter layer **152** may improve device reliability by trapping oxygen and moisture that otherwise can degrade performance of the organic x-ray detector **100**.

In some embodiments, an x-ray system **200** is also presented. As shown in FIG. **17**, the x-ray system **200** includes an x-ray source **210** configured to irradiate an object **220** with x-ray radiation see figures, an organic x-ray detector **100** as described earlier, and a processor **230** operable to process data from the organic x-ray detector **100**. FIGS. **18A** and **18B** further show embodiments of the x-ray system **200** suitable for substantially flat objects or objects with a curved shape. As shown in FIGS. **18A** and **18B**, the organic x-ray detector **100** may have a shape suitable for the object **220**. In FIGS. **18A** and **18B**, the processor **230** may be communicatively coupled to the organic x-ray detector **100** using a wired or a wireless connection.

An organic x-ray detector **100** according to embodiments of the present invention may be used in imaging systems, for example, in conformal imaging, with the organic x-ray detector **100** in intimate contact with the imaging surface. For parts with internal structure, the organic x-ray detector **100** may be rolled or shaped to contact the part being imaged. Applications for the organic x-ray detectors according to embodiments of the present invention include security imaging; medical imaging; and industrial and military imaging for pipeline, fuselage, airframe and other tight access areas.

EXAMPLES

Comparative Example 1

X-Ray Detector Imager without Oxygen or
Moisture Getter Layers

Glass based thin-film-transistor (TFT) array pre-coated with ITO was used as the substrate. A hole-transport layer was deposited onto ultraviolet-ozone treated TFT array substrates via spin-coating and then baked on a hotplate. An absorber layer consisting of a fullerene based acceptor and a donor material was then spin-coated on top of the hole-transport layer inside of a N₂ purged glovebox. The imager fabrication was completed with sputtering of the ITO cathode. Next the DRZ-Plus scintillator (Mitsubishi Chemical) made of gadolinium sulfoxylate doped with terbium (Gd₂O₂S:Tb) was laminated to the imager using a pressure sensitive adhesive (PSA) film from 3M under the product name of 8191L. The imager was encapsulated using a cover glass and an edge sealant.

Example 1

X-Ray Detector Imager with a Moisture Getter
Layer

The imager prepared in Example 1 was sealed in the same way as Comparative Example 1 except with the incorpora-

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tion of a moisture getter, DryFlex, which was purchased from SAES Getters Group.

Example 2

X-Ray Detector Imager with an Oxygen Getter
Layer

The imager prepared in Example 2 was sealed in the same way as Comparative Example 1 except with the incorporation of an oxygen getter, poly(ethylene glycol) 600 diacrylate, which was purchased from Sartomer under the product name of SR610 and mixed with the cobalt(II) acetate tetrahydrate catalyst and 1% by weight Irgacure 819 photoinitiator. The SR610-based oxygen getter layer was cured under UV irradiation.

Example 3

X-Ray Detector Imager with Both the Oxygen and
Moisture Getter Layers

The imager prepared in Example 3 was sealed in the same way as Comparative Example 1 except with the incorporation of both the oxygen getter layer of Example 2 and the moisture getter of Example 1. The layers had a configuration similar to that of FIG. **11**.

Comparative Example 2

X-Ray Detector Imager without Oxygen or
Moisture Getter Layers

The imager prepared in Comparative Example 2 was prepared in the same way as Comparative Example 1 except that it further included an organic smoothing layer; and an ITO barrier coating between the ITO cathode and the scintillator layer. The organic smoothing layer consisting of a UV cross-linkable acrylate was applied on top of the ITO via screen printing and UV cured. The ITO moisture barrier layer was then sputtered on top of the smoothing layer.

Example 4

X-Ray Detector Imager with a Moisture Getter
Layer

The imager prepared in Example 4 was prepared in the same way as Comparative Example 2 except with the incorporation of a moisture getter, DryFlex, which was purchased from SAES Getters Group.

Example 5

X-Ray Detector Imager with Both the Oxygen the
Moisture Getter Layers

The imager prepared in Example 5 was sealed in the same way as Comparative Example 2 except with the incorporation of both the oxygen getter layer of Example 2 and the moisture getter of Example 1. The layers had a configuration similar to that of FIG. **11**.

Reliability of the imagers was then tested at 85° C. and 85% relative humidity. Performance was characterized using x-ray imager functional tester. The increase in the number of defects is summarized in Table 1 and Table 2. As one can see, incorporating getter materials s reduced the change in

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defect counts and improved imager stability. Further the increase in number of defects reduced significantly when both the getter layers were used.

TABLE 1

| Increase in number of defects for imagers with and without getter materials | | | | |
|--|--------------------|------------------|------------------------|-------------------------------------|
| Example | Moisture Getter | Oxygen Getter | Hours at 85° C./85% | Increase in number of defects |
| Comparative Example 1 | No | No | 336 | 57 |
| Example 1 | Yes | No | 336 | 39 |
| Example 2 | No | Yes | 336 | 46 |
| Example 3 | Yes | Yes | 336 | 5 |

TABLE 2

| Increase in number of defects for imagers with and without getter materials | | | | |
|--|--------------------|------------------|------------------------|-------------------------------------|
| Example | Moisture Getter | Oxygen Getter | Hours at 85° C./85% | Increase in number of defects |
| Comparative Example 2 | No | No | 576 | 93 |
| Example 4 | Yes | No | 505 | 0 |
| Example 5 | Yes | Yes | 562 | 0 |

The foregoing examples are merely illustrative, serving to exemplify only some of the features of the invention. The appended claims are intended to claim the invention as broadly as it has been conceived and the examples herein presented are illustrative of selected embodiments from a manifold of all possible embodiments. Accordingly, it is the Applicants' intention that the appended claims are not to be limited by the choice of examples utilized to illustrate features of the present invention. As used in the claims, the word "comprises" and its grammatical variants logically also subtend and include phrases of varying and differing extent such as for example, but not limited thereto, "consisting essentially of" and "consisting of." Where necessary, ranges have been supplied; those ranges are inclusive of all sub-ranges there between. It is to be expected that variations in these ranges will suggest themselves to a practitioner having ordinary skill in the art and where not already dedicated to the public, those variations should where possible be construed to be covered by the appended claims. It is also anticipated that advances in science and technology will make equivalents and substitutions possible that are not now contemplated by reason of the imprecision of language and these variations should also be construed where possible to be covered by the appended claims.

The invention claimed is:

1. An x-ray detector, comprising:

a layered structure comprising:

a substrate,

a thin-film transistor (TFT) array disposed on the substrate,

an organic photodiode disposed on the TFT array, and

a scintillator layer disposed on the organic photodiode; an encapsulation cover at least partially encapsulating the layered structure; and

at least one of a moisture getter layer and an oxygen getter layer disposed proximate to the organic photodiode, and in the path of an x-ray radiation incident on the layered structure.

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2. The x-ray detector of claim 1, wherein the moisture getter layer and the oxygen getter layer are disposed as two or more separate layers.

3. The x-ray detector of claim 1, wherein the layered structure comprises at least one of the moisture getter layer and the oxygen getter layer.

4. The x-ray detector of claim 3, wherein the layered structure comprises both the moisture getter layer and the oxygen getter layer.

5. The x-ray detector of claim 3, wherein at least one of the moisture getter layer and the oxygen getter layer is interposed between the organic photodiode and the scintillator layer.

6. The x-ray detector of claim 3, wherein at least one of the moisture getter layer and the oxygen getter layer is disposed on the scintillator layer.

7. The x-ray detector of claim 1, wherein at least one of the moisture getter layer and the oxygen getter layer substantially encapsulates the layered structure.

8. The x-ray detector of claim 1, wherein at least one of the moisture getter layer and the oxygen getter layer is disposed in contact with at least a portion of the encapsulation cover.

9. The x-ray detector of claim 8, wherein the oxygen getter layer is disposed in contact with at least a portion of the encapsulation cover, and the moisture getter layer is disposed in contact with the oxygen getter layer.

10. The x-ray detector of claim 1, wherein the layered structure comprises the oxygen getter layer and the moisture getter layer is disposed in contact with at least a portion of the encapsulation cover.

11. The x-ray detector of claim 1, wherein the moisture getter layer comprises alkali metals, alkaline metals, alkali metal oxides, alkaline metal oxides, aluminum oxide, zeolite, silica, or combinations thereof.

12. The x-ray detector of claim 1, wherein the oxygen getter layer comprises polyethers, crown ethers, ascorbic acid, polyhydric alcohols, alkylene glycols, or combinations thereof.

13. The x-ray detector of claim 1, wherein the substrate comprises a material selected from the group consisting of glass, metal foil, plastic, and combinations thereof.

14. The x-ray detector of claim 1, wherein the TFT array comprises a silicon TFT array, an oxide TFT array, an organic TFT, or combinations thereof.

15. An x-ray detector, comprising:

a layered structure comprising:

a substrate,

a thin-film transistor (TFT) array disposed on the substrate,

an organic photodiode disposed on the TFT array, and

a scintillator layer disposed on the organic photodiode;

an encapsulation cover at least partially encapsulating the layered structure;

an oxygen getter layer disposed between the organic photodiode and the scintillator layer in the layered structure; and

a moisture getter layer disposed in contact with at least a portion of the encapsulation cover.

16. An x-ray system, comprising:

an x-ray source;

an x-ray detector comprising:

a layered structure comprising:

a substrate,

a thin-film transistor (TFT) array disposed on the substrate,

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an organic photodiode disposed on the TFT array,
and
a scintillator layer disposed on the organic photo-
diode;
an encapsulation cover at least partially encapsulating 5
the layered structure; and
at least one of a moisture getter layer and an oxygen
getter layer disposed proximate to the organic pho-
todiode, and in the path of an x-ray radiation incident
on the layered structure; and 10
a processor operable to process data from the X-ray
detector.

17. The x-ray system of claim **16**, wherein the layered
structure comprises at least one of the moisture getter layer
and the oxygen getter layer. 15

18. The x-ray system of claim **16**, wherein at least one of
the moisture getter layer and the oxygen getter layer is
disposed in contact with at least a portion of the encapsu-
lation cover.

19. The x-ray system of claim **16**, wherein the moisture 20
getter layer and the oxygen getter layer are disposed as two
or more separate layers.

20. The x-ray system of claim **16**, wherein the layered
structure comprises the oxygen getter layer and the moisture
getter layer is disposed in contact with at least a portion of 25
the encapsulation cover.

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